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BORON-NITRIDE AND ITS PRECURSORS(U) ULTRASYSTEMS

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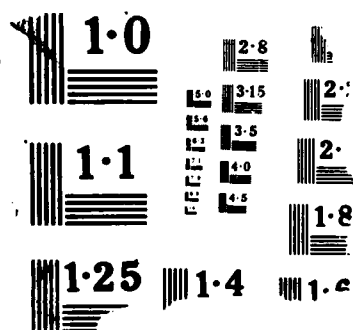
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Boron-Nitride and Its Precursors

by

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# Boron Nitride and Its Precursors

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Stepwise condensation of a series of borazines was investigated. The compounds studied were B-trichloro-N-triphenylborazine, B-triamino-N-triphenylborazine, B-trianilinoborazine, B-tris[di(trimethylsilyl)amino]-borazine, B-trichloro-N-tris(trimethylsilyl)borazine, and B-triamino-N-tris(trimethylsilyl)borazine. The formation of preceramic polymers occurs by ring opening mechanism which leads to singly and doubly joined borazine rings. This process requires the presence of a combined total of six protons on the ring and exocyclic nitrogens. Compounds where this arrangement is absent, B-trichloro-N-triphenylborazine, B-tris[di(trimethylsilyl)amino]borazine, and B-trichloro-N-tris(trimethylsilyl)borazine, failed to undergo condensation to any significant degree. Materials obtained from the phenyl-substituted borazines gave essentially nonprocessable polymers on pyrolysis; from B-triamino-N-tris(trimethylsilyl)borazine, preceramic polymers amenable to fiber manufacture were obtained. Investigation of potential linear precursor to boron-nitrogen polymers resulted in the synthesis of  $\mu$ -imido-bis[bis(trimethylsilyl)aminotrimethylsilylamino]borane (I) and  $\mu$ -oxo-bis[bis(trimethylsilyl)aminotrimethylsilylamino]borane (II). The crystal structures of the two compounds were essentially identical with the exception of the bridging atoms and their immediate environments. The same applied to mass spectral breakdown patterns wherein the major fragments differed by one amu, with the exception of the ion  $332^+$  which is characteristic to the oxygen-bridged compound.

Refractories such as boron nitride, silicon nitride, silicon carbide, and boron carbide are of great importance for the production or protection of systems which can be operated in very high

temperature environments. The applicability of these materials as coatings, fibers, as well as bulk items depends on the ability to produce a readily processible polymer, which can be formed into the desired shape of the final item prior to exhaustive pyrolysis and transformation into a ceramic. The technology to provide such precursors for silicon carbide, silicon nitride, and graphite, in particular the latter, has been developed and although work is proceeding on improvements, the premises are relatively well established (1). The situation in the case of boron nitride is entirely different. The extensive work performed in the sixties was directed at thermally stable polymers. The products were poorly characterized and the literature data are conflicting (2). More recently, claims have been made to the synthesis of BN preceramic polymers amenable to fiber production using the pyrolysis of B-triamino-N-triphenylborazine (3). Unfortunately, this work could not be reproduced (4,5).

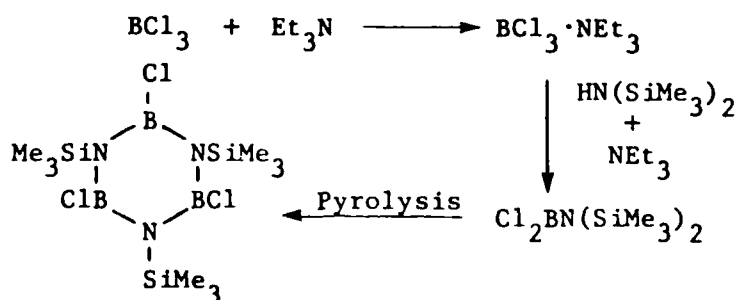
Boron nitride, in view of its unique properties, namely absence of electrical conductivity, oxidation resistance, optical transparency, and high neutron capture cross-section for special applications, offers advantages over other ceramics. Thus, for the past several years the group at Ultrasystems has been actively involved in investigating routes leading to preceramic BN polymers using both cyclic and linear starting materials. Some of the findings generated will be discussed.

## Results and Discussion

**Borazine synthesis.** The ease of borazine ring condensation would be expected to depend on the nature of the substituents. To investigate these aspects, a series of compounds were synthesized, namely B-trichloro-N-triphenylborazine, B-triamino-N-triphenylborazine, B-trianilinoborazine, B-tris[di(trimethylsilyl)amino]borazine, B-trichloro-N-tris(trimethylsilyl)borazine, and B-triamino-N-tris(trimethylsilyl)borazine.

B-trichloro-N-triphenylborazine, mp 290-292°C, was obtained in 86% yield following the procedure of Groszos and Stafiej (6). This material was then transformed into B-triamino-N-triphenylborazine in 67% yield using the method of Toeniskoetter and Hall (7). B-trianilinoborazine and the novel B-tris[di(trimethylsilyl)amino]borazine (mp. 131.5-132°C; characterized by GC/MS, molecular ion 558 amu, and elemental analysis) were synthesized in 76 and 71% yields, respectively, by interaction of aniline and hexamethyldisilazane with chloroborazine in the presence of triethylamine.

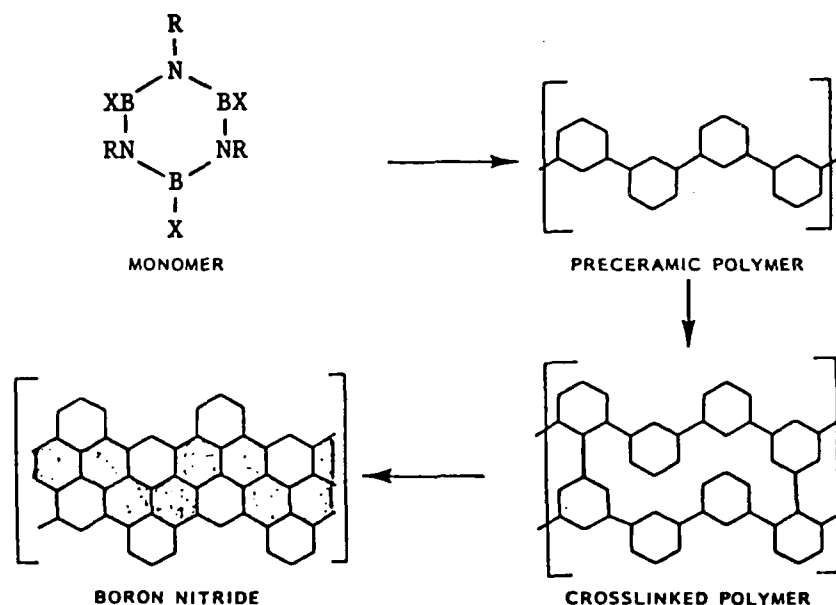
The synthesis of B-trichloro-N-tris(trimethylsilyl)borazine was much more complicated than that of the other borazines. The overall scheme is given below:



Boron trichloride-triethylamine adduct, mp 89-91°C, was obtained in 80% yield following essentially the procedure of Ohashi, et al. (8). The product was washed with methanol, but not crystallized from it. It was found that crystallization from dilute ethanol reported by Gerrard, Lappert, and Pearce (9) caused extensive degradation. Bis(trimethylsilyl)aminodichloroborane was prepared following the procedure of Wells and Collins (10).

The pyrolysis of bis(trimethylsilyl)aminodichloroborane to B-trichloro-N-tris(trimethylsilyl)borazine, contrary to literature (11), did not take place in boiling xylene. Temperatures above 150°C were necessary for trimethylchlorosilane elimination. The highest yield of the relatively pure product was around 20%. The transformation of the B-trichloro-N-tris(trimethylsilyl)borazine to B-triamino-N-tris(trimethylsilyl)borazine proceeded readily using liquid ammonia.

Borazine Pyrolysis Studies. In a simplistic manner, one can visualize the formation of boron nitride via stepwise eliminations between rings, i.e.,



giving initially the "linear" preceramic polymer, then the lightly crosslinked structure B, followed by a partial B-N system, C, and finally pure boron nitride. The pyrolysis techniques utilized were fully described previously (4) and thus will not be reiterated here. The potential borazine candidates can be broadly divided into two classes of materials, one where the substituent on the ring boron is nitrogen-free, e.g., a halogen, and the second where the substituent is an amino moiety. With respect to the suitability of any given borazine, the important aspects are the ease of formation of the leaving molecule and its volatility. In this respect, B-trichloro-N-tris(trimethylsilyl)borazine would seem an ideal candidate. Unfortunately, pyrolysis at 260°C liberated only 6.1% of the expected trimethylchlorosilane; 75% of the starting material was recovered. Heating at 360°C for 19 h resulted in 56.0% yield of trimethylchlorosilane and a glassy residue. Further heating at

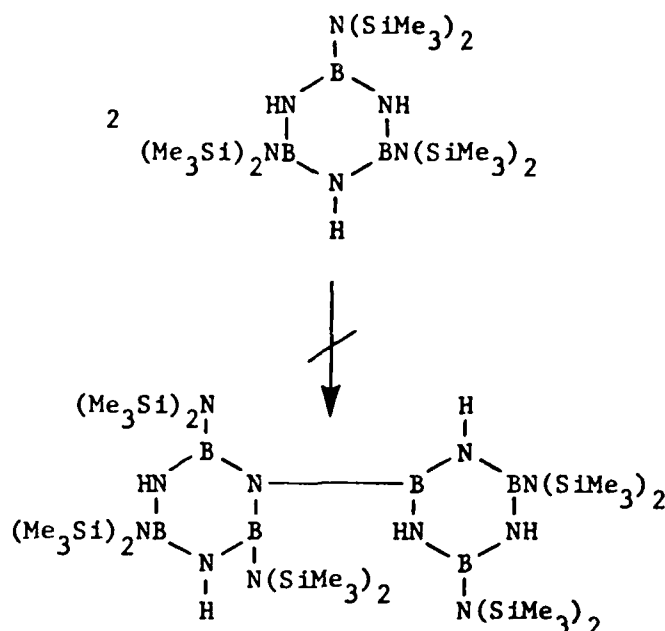
360°C for 72 h afforded only an additional 7.3% of the expected trimethylchlorosilane. This result shows clearly that this type of borazine does not lead to a desirable preceramic polymer, inasmuch as at 260°C the condensation process proceeds only to a limited degree, with the starting material being largely recovered and the polymeric product formed being both insoluble and infusible. B-trichloro-N-triphenylborazine would not be expected to undergo condensation readily inasmuch as the formation of chlorobenzene is not a favored process. The experimental data supported this postulation; essentially no degradation occurred at 300°C.

B-triamino-N-triphenylborazine, and in particular its isomer, B-trianilinoborazine, the latter either alone or in co-reaction with B-triamino-N-triphenylborazine, gave fusible, <200°C, and organic solvent soluble preceramic polymers after exposure to temperatures below 250°C (4,5). However, in particular using B-triamino-N-triphenylborazine alone, the process was irreproducible; nonfusible products were obtained. In this system, carbon retention was invariably observed after exposure to 1000°C, contrary to the Japanese claims (3).

The thermal degradation of B-trianilinoborazine, when conducted in ammonia even below 215°C, produced 87.7% of the available aniline. This was brought up to 92.3% by further pyrolysis at 275-299°C which compares with the maximum of 53% observed under the same heating regime in nitrogen atmosphere (4). Thus, it is obvious that the presence of ammonia facilitates the elimination process. However, since 31% of the aniline evolved was replaced by ammonia, based on the weight of the residue, the degree of condensation was not as high as would appear from the aniline collected. Due to the materials' insolubility in organic solvents, the molecular weights could not be determined.

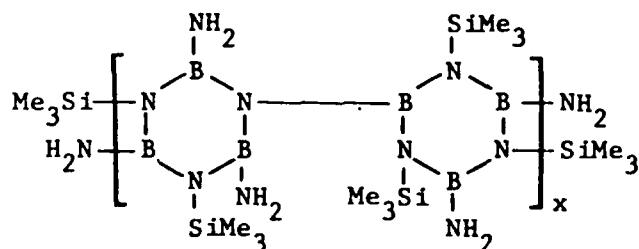
From the investigations of the phenylaminoborazines it was established that the condensation does occur via ring opening (4), postulated earlier by Toeniskoetter and Hall (7), followed by elimination and bridge formation. Isomerization is inherently associated with this mechanism, as illustrated in Scheme 1. For this process to take place, it is necessary that the boron substituent is either a  $\text{NH}_2$  or  $\text{NHR}$  moiety. Namely, the ring opening mechanism requires the presence of a combined total of six protons on the ring and exocyclic nitrogens. In agreement with the above, B-tris[di(trimethylsilyl)amino]borazine, which contains only three hydrogens, was recovered unchanged after exposure to 410°C for 89 h. One could visualize here the intermolecular condensation to occur, in the absence of ring opening, with elimination of hexamethyldisilazane, e.g.,





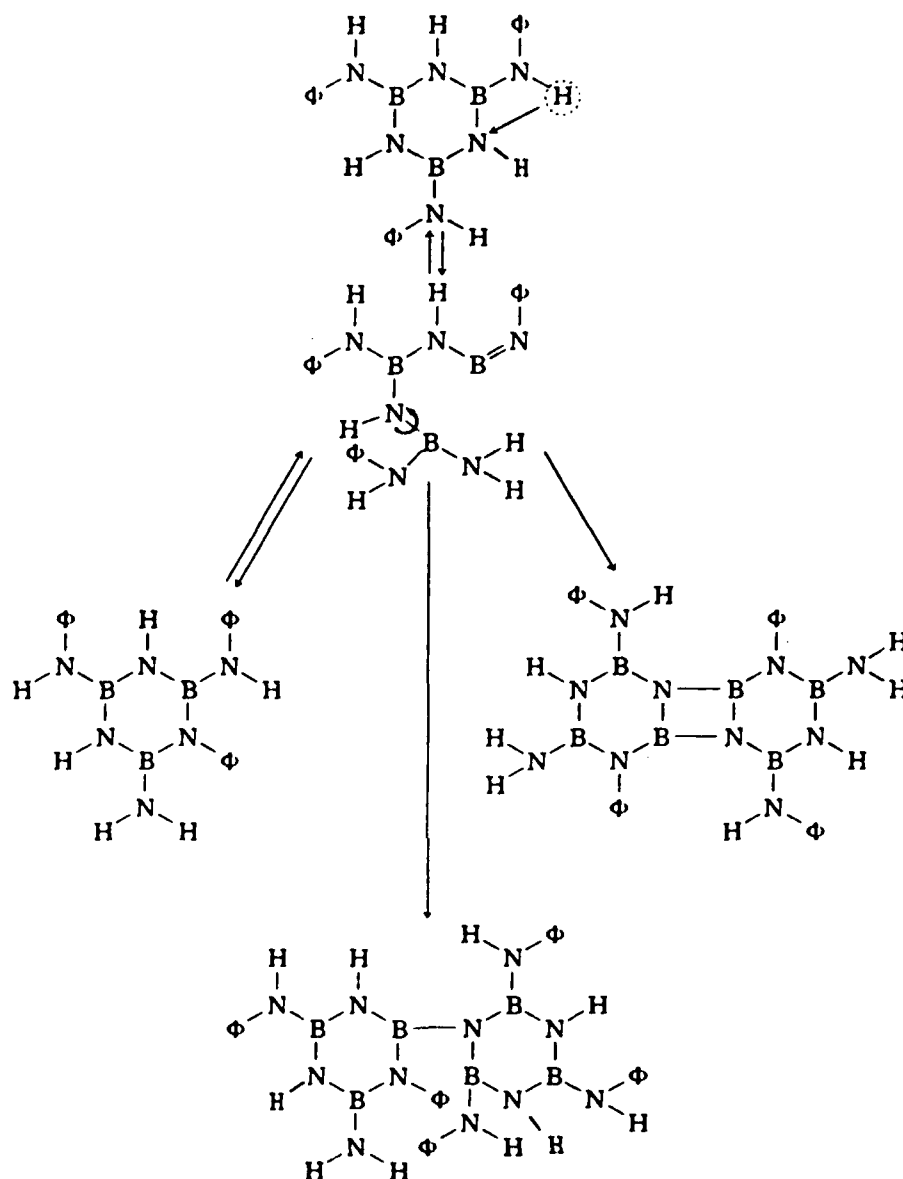
This apparently is not the case. On prolonged exposure in ammonia at 250-260°C some liberation of hexamethyldisilazane took place, but only to a very low degree.

The behavior of B-triamino-N-tris(trimethylsilyl)borazine was in good agreement with the ring opening mechanism. This compound was much more reactive than its phenyl analogues; thus, the pure monomer could not be isolated. The product obtained from the interaction of ammonia and B-trichloro-N-tris(trimethylsilyl)borazine consisted of a 1:1 mixture of the monomer and a singly-bridged dimer,  $x=1$ .

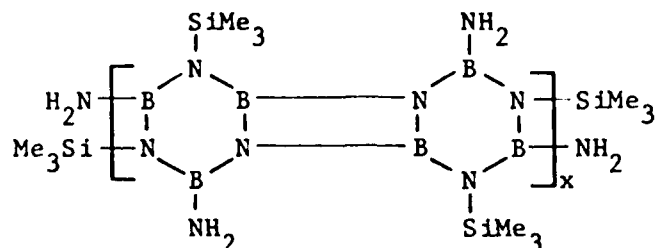


Both the monomer and dimer were composed most likely of isomers with some protons residing on ring nitrogens and with the  $\text{NHSiMe}_3$  moiety replacing the amino group on some of the boron ring atoms in accordance with the Scheme 1. This assumption is supported by the liquid nature of the product and its infrared spectrum which exhibited two broad bands centered at 3430 and 3530  $\text{cm}^{-1}$ . The infrared spectrum of pure B-triamino-N-tris(trimethylsilyl)borazine would be expected to be similar to that of B-triamino-N-tris(triphenyl)borazine where three sharp bands at 3430, 3505, and 3530 were observed (4). In the latter case, once the condensation process was initiated, the sharp bands disappeared (4).

Scheme I

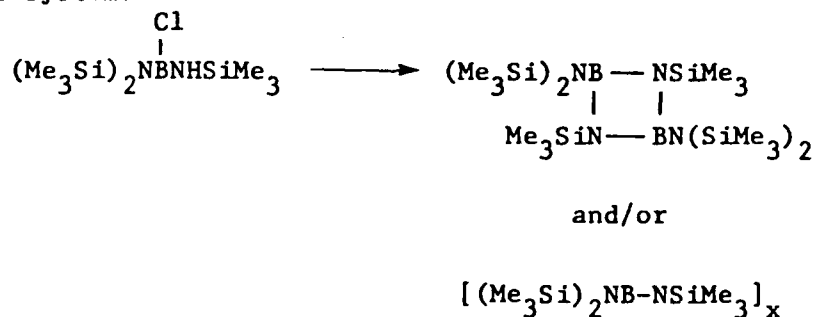


To remove volatile impurities, the material was heated in vacuo at  $135^\circ\text{C}$ . This treatment resulted in further condensation. Thus, the distillation residue was composed of a mixture of doubly-bridged dimers and tetramers,  $x=1$  and 2 as determined from the molecular weight, boron and nitrogen analyses, and the volatile condensibles produced.

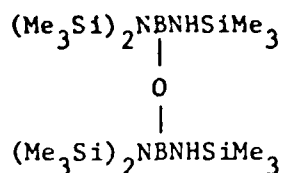


The condensation process apparently involves elimination of trimethylsilylamine,  $(\text{CH}_3)_3\text{SiNH}_2$ , which, being unstable, disproportionates into hexamethyldisilazane and ammonia. In the condensible volatiles collected, these materials were present in a 1:1 ratio supporting the postulated process. Further thermolysis at  $200^\circ\text{C}$  (52 h), followed by 4 h at  $250\text{--}260^\circ\text{C}$ , resulted in a mixture of doubly-bridged tetramers and octamers,  $x=2$  and 4. At this stage, 53% of the potential leaving groups were liberated. From the tetramer/octamer mixture, fibers with  $10\text{--}20\ \mu$  diameter could be melt drawn as shown in Figures 1 and 2. Gradual heat treatment in ammonia, from  $65\text{--}950^\circ\text{C}$ , resulted in white, pure boron nitride fibers. The fibers exhibited no weight loss under thermogravimetric conditions, both in air and in nitrogen up to  $1000^\circ\text{C}$  (12).

Potential Non-Cyclic Precursors of Preceramic Polymers. Boranes such as bis(trimethylsilyl)aminotrimethylsilylaminochloroboranes can be viewed as monomers for preceramic polymer and, ultimately, boron nitride production. Intermolecular dehydrohalogenation of this borane would be thus expected to yield either the dimer or the polymeric system.

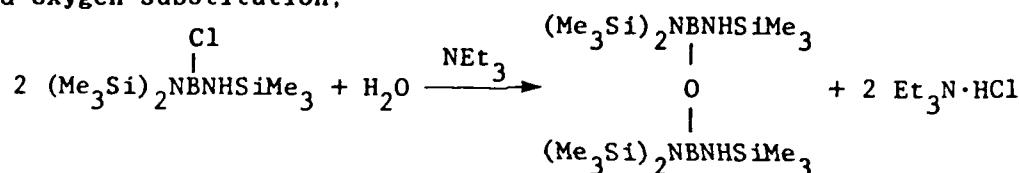


Bis(trimethylsilyl)aminotrimethylsilylaminochloroborane was obtained in a 70% yield following the procedure of Wells and Collins (10). No triethylamine hydrochloride was formed and the starting material was recovered unchanged after prolonged refluxing with a five-fold excess of specially dried triethylamine. However, when the triethylamine employed was not so rigorously dried and 10- to 20-fold excess was used, an oxygen-bridged compound,

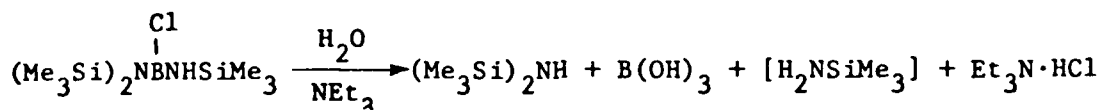


II

was obtained in a 35% yield. Conducting the reaction in benzene using the required quantity of water in the presence of triethylamine gave 55% yield of triethylamine hydrochloride, but only a 7% yield of the oxygen-bridged product. The surprising finding was the relatively high yield (~18%) of material which is either  $(\text{Me}_3\text{SiNH})_2\text{BN}(\text{SiMe}_3)_2$  or  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{BNH}_2$  (the differentiation could not be made from the mass spectral fragmentation pattern), together with hexamethyldisilazane and amino-bis(trimethylsilyl)aminotrimethylsilylaminoborane,  $(\text{Me}_3\text{Si})_2\text{NB}(\text{NH}_2)\text{NHSiMe}_3$ , or its isomer,  $\text{B}(\text{NHSiMe}_3)_3$ . These products were also observed, but in low concentrations, in the reaction where the high yield of the oxygen-bridged compound was realized. The major difference between these reactions was the relative ratio of triethylamine and the presence of benzene. Based on these results, it is clear that the process involving hydrogen chloride elimination and oxygen substitution,

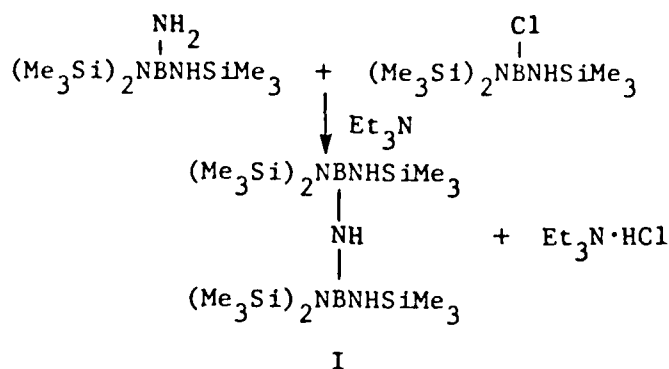


is not the only one occurring. Apparently, a more extensive hydrolysis of the chloroborane takes place concurrently, i.e.,



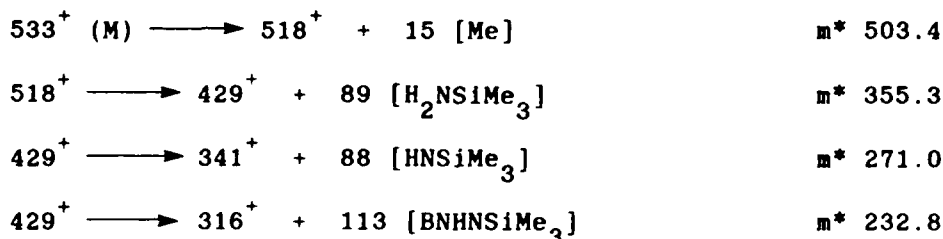
Inasmuch as trimethylsilylamine is unstable, it will decompose into ammonia and hexamethyldisilazane. The ammonia thus formed could be visualized to form the amino compound  $(\text{Me}_3\text{Si})_2\text{NB}(\text{NH}_2)\text{NHSiMe}_3$ . Since  $(\text{Me}_3\text{Si})_2\text{NB}(\text{NHSiMe}_3)_2$  was prepared by Wells and Collins (13) via interaction of the chloroborane with hexamethyldisilazane, its production here could follow the same path.

The nitrogen-bridged analogue,  $[(\text{Me}_3\text{Si})_2\text{NBNHSiMe}_3]_2\text{NH}$ , Compound I, was formed in a 57% yield from bis(trimethylsilyl)aminotrimethylsilylaminoborane and aminobis(trimethylsilyl)aminotrimethylsilylaminoborane in the presence of triethylamine by heating at 100°C over an 18 h period, i.e.

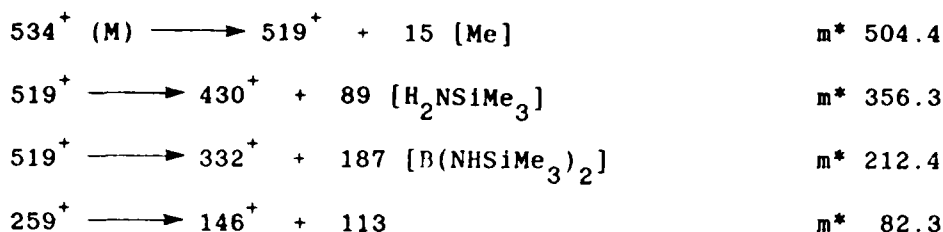


The nitrogen-bridged compound exhibited physical and spectral characteristics very similar to those of the oxygen-bridged compound. This is illustrated by the close melting points (169-171°C and 158-160°C, respectively) and essentially identical IR spectra (the spectrum of  $\mu$ -imido-bis[bis(trimethylsilyl)aminotrimethylsilylamino]borane is given in Figure 3). Thermal behavior of I and II is also similar as shown by DSC traces, where in the oxygen-bridged compound two strong endotherms were observed at 70 and 75°C and in the nitrogen-bridged material at 85 and 105°C. No phase transition responsible for these endotherms could be visually observed on heating. Both materials, on remelting in air, exhibited the same melting points as those obtained under inert conditions pointing to their thermal, oxidative, and hydrolytic stabilities. Investigation of the condensation reactions of Compound I are currently in progress.

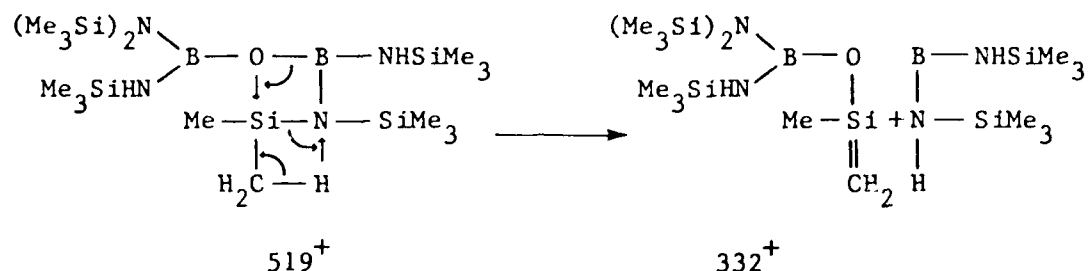
The mass spectral breakdown patterns for the two bridged compounds were very similar, with the exception that the peaks were one mass unit higher in the case of the oxygen-bridged material. Both compounds produced strong molecular ions at 533<sup>+</sup> (I) and 534<sup>+</sup> (II). The processes responsible for several of the major fragments could be identified from the metastables. In the case of  $\mu$ -imido-bis[bis(trimethylsilyl)aminotrimethylsilylamino]borane, these are:



In view of the absence of the additional proton, the equivalent of the 341<sup>+</sup> ion, namely the 342<sup>+</sup> ion, would not be expected to be formed to any significant extent in the case of the oxygen-bridged compound. The fragmentation pattern confirms it and no metastable for this process was found. In the oxygen-bridged compound, metastables were observed at m/e 504.5, 357.5, 213, and 82.5. The processes responsible have been identified as:



The  $332^+$  ion is specific to the oxygen-bridged product. It is speculated that it is formed by the following path from the  $519^+$  ion:



In order to obtain insight into the nature of bonding in catenated BN species, the crystal and molecular structures of Compounds I and II were obtained. Both compounds crystallize isomorphously in the monoclinic space group  $P2_1/n$ . For I,  $a = 12.876(2) \text{ \AA}$ ,  $b = 14.828(3) \text{ \AA}$ ,  $c = 18.628(4) \text{ \AA}$ ;  $\beta = 97.07(2)^\circ$ ;  $V = 3529(1) \text{ \AA}^3$ ;  $Z = 4$ , and the molecular weight based on a calculated density of  $1.005 \text{ g/cm}^3$  was 533.85, in excellent agreement with the molecular ion observed in the mass spectrum (533 m/e). Refinement led to  $R_f = 4.1\%$  and  $R_{wf} = 4.2\%$  for 5093 independent reflections. The structure of I, given in Figure 4, confirms the presence of a central  $\text{N}_2\text{BNBN}_2$  framework that is essentially planar with a  $\text{B}(1)\text{-N}(1)\text{-B}(2)$  angle of  $135.9(2)^\circ$ . The remaining B-N-B angles are close to  $120^\circ$ . The B-N bond distances reflect a competition for  $\pi$ -electron density. The shortest B-N bonds,  $\text{B}(2)\text{-N}(5)$   $1.405(3) \text{ \AA}$  and  $\text{B}(1)\text{-N}(3)$   $1.423(3) \text{ \AA}$ , are to nitrogens bonded to one silicon, while the longest B-N bonds  $\text{B}(2)\text{-N}(4)$   $1.485(3) \text{ \AA}$  and  $\text{B}(1)\text{-N}(2)$   $1.487(3) \text{ \AA}$  are to nitrogens bonded to two silicons. For II,  $a = 12.826(3) \text{ \AA}$ ,  $b = 14.822(4) \text{ \AA}$ , and  $c = 18.557(4) \text{ \AA}$ ;  $\beta = 95.98(2)^\circ$ ;  $V = 3509(1) \text{ \AA}^3$ ;  $Z = 4$ , F.W. = 534.8 amu, and the calculated density is  $1.012 \text{ g/cm}^3$ . Refinement led to  $R_f = 4.3\%$  and  $R_{wf} = 4.0\%$  for 4458 independent reflections. Structure II, given in Figure 5, differs from I only in the existence of a central B-O-B unit wherein the boron oxygen distances [ $\text{B}(1)\text{-O}(1)$   $1.380(3)$  and  $\text{B}(2)\text{-O}(1)$   $1.389(3)$ ] are somewhat shorter than the corresponding B-N distances for I [ $\text{B}(1)\text{-N}(1)$   $1.428(3)$  and  $\text{B}(2)\text{-N}(1)$   $1.446(3)$ ].

#### Acknowledgment

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11. Geymayer, P., Rochow, E. G. Monatsh. 1966, 97, 429.
12. Without additional heat treatment above 1000°C (annealing), the fibers are amorphous based on transmission electron microscopy (TEM) with islands of microfibrils or microcrystallites. Selected area electron diffraction (SAED) of the microcrystallites indicates that they could be BN, B<sub>2</sub>O<sub>3</sub>, or graphite. Auger electron spectroscopy showed the fibers to be essentially free of carbon which is supported by their colorless appearance. X-ray diffraction produces a weak signal corresponding to hexagonal BN. The fact that the fibers do not change in shape when heated at 1000°C rules out the presence of significant amounts of B<sub>2</sub>O<sub>3</sub>, which melts at 460°C. Further characterization of the fibers in regard to composition, structure, susceptibility to "graphitization", as well as strength and density is in progress.
13. Wells, R. L., Collins, A. L. Inorg. Chem. 1968, 7, 419.

Figure 1. Melt spun BN precursor fibers, magnification 500x.

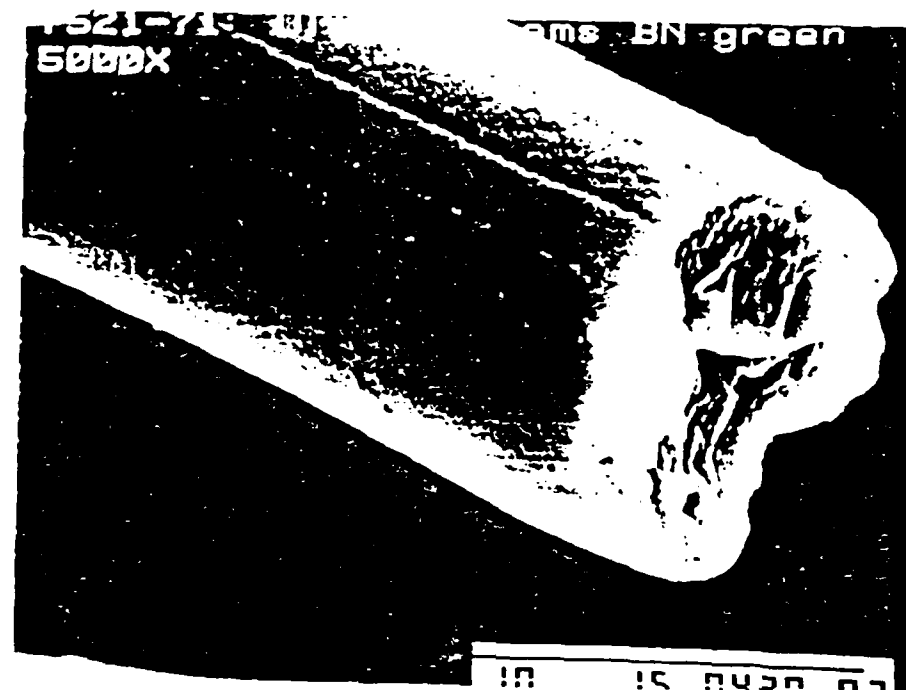
Figure 2. Melt spun BN precursor fibers, magnification 5,000x.

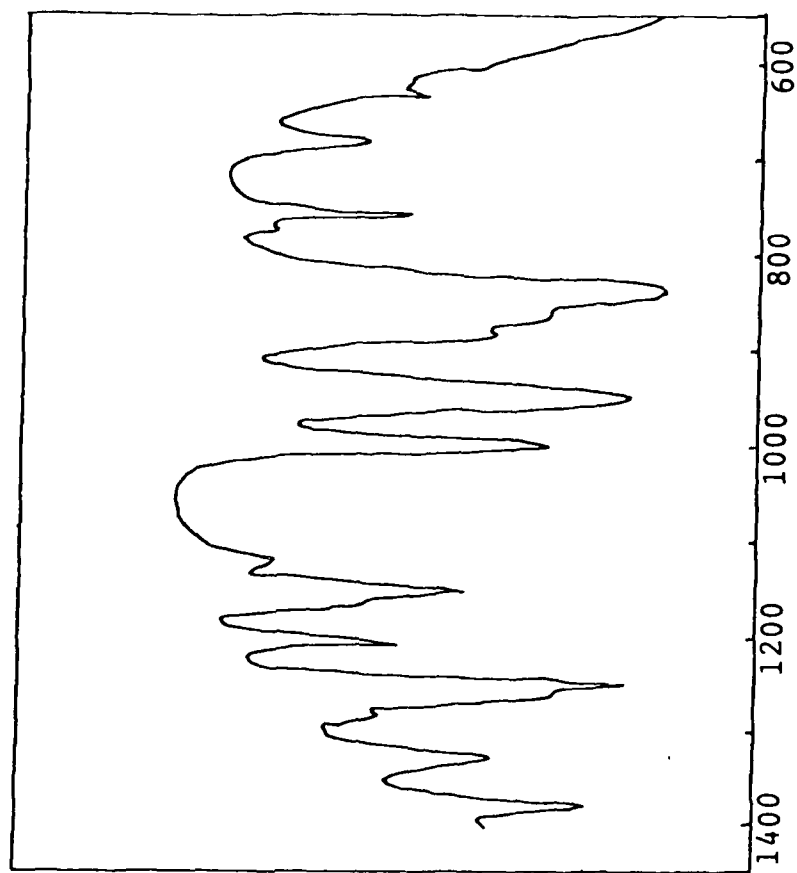
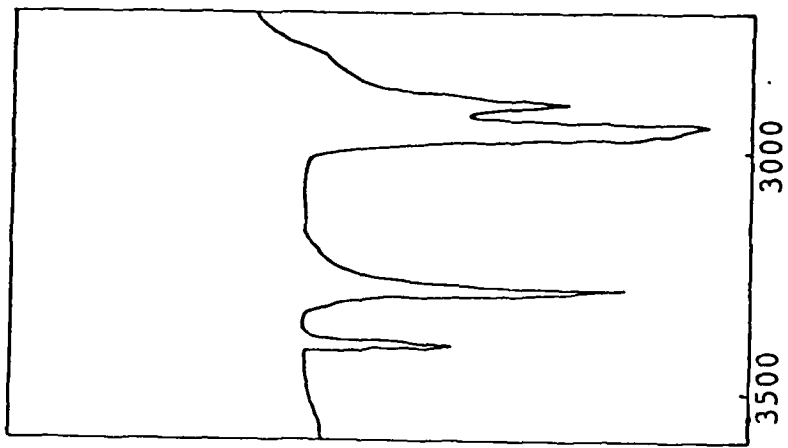
Figure 3. Infrared spectrum of  $\mu$ -imido-bis[bis(trimethylsilyl)-aminotrimethylsilylamino]borane (I).

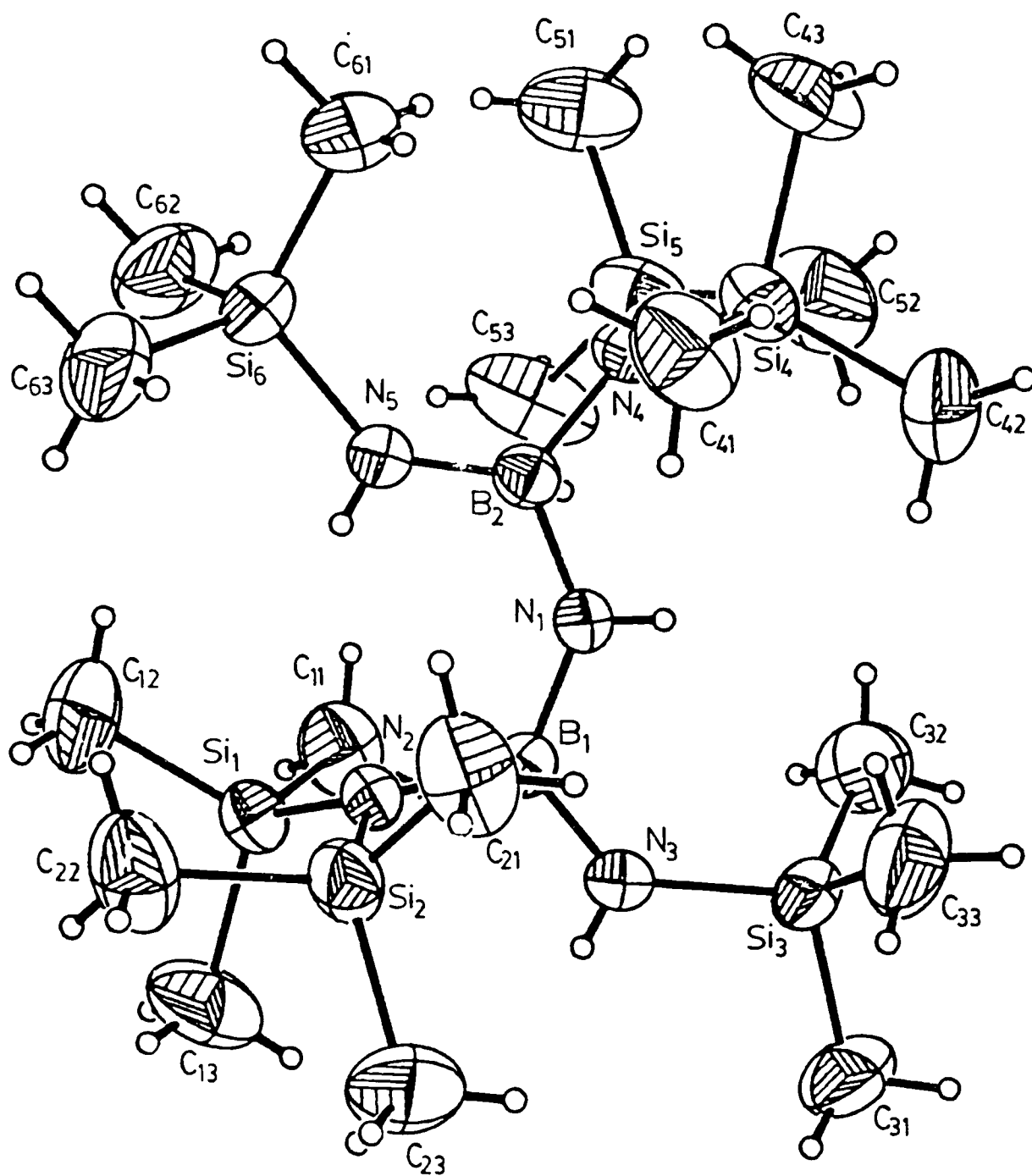
Figure 4. A perspective drawing of  $C_{18}H_{57}N_5Si_6B_2$  with nonhydrogen atoms represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density; hydrogen atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion.

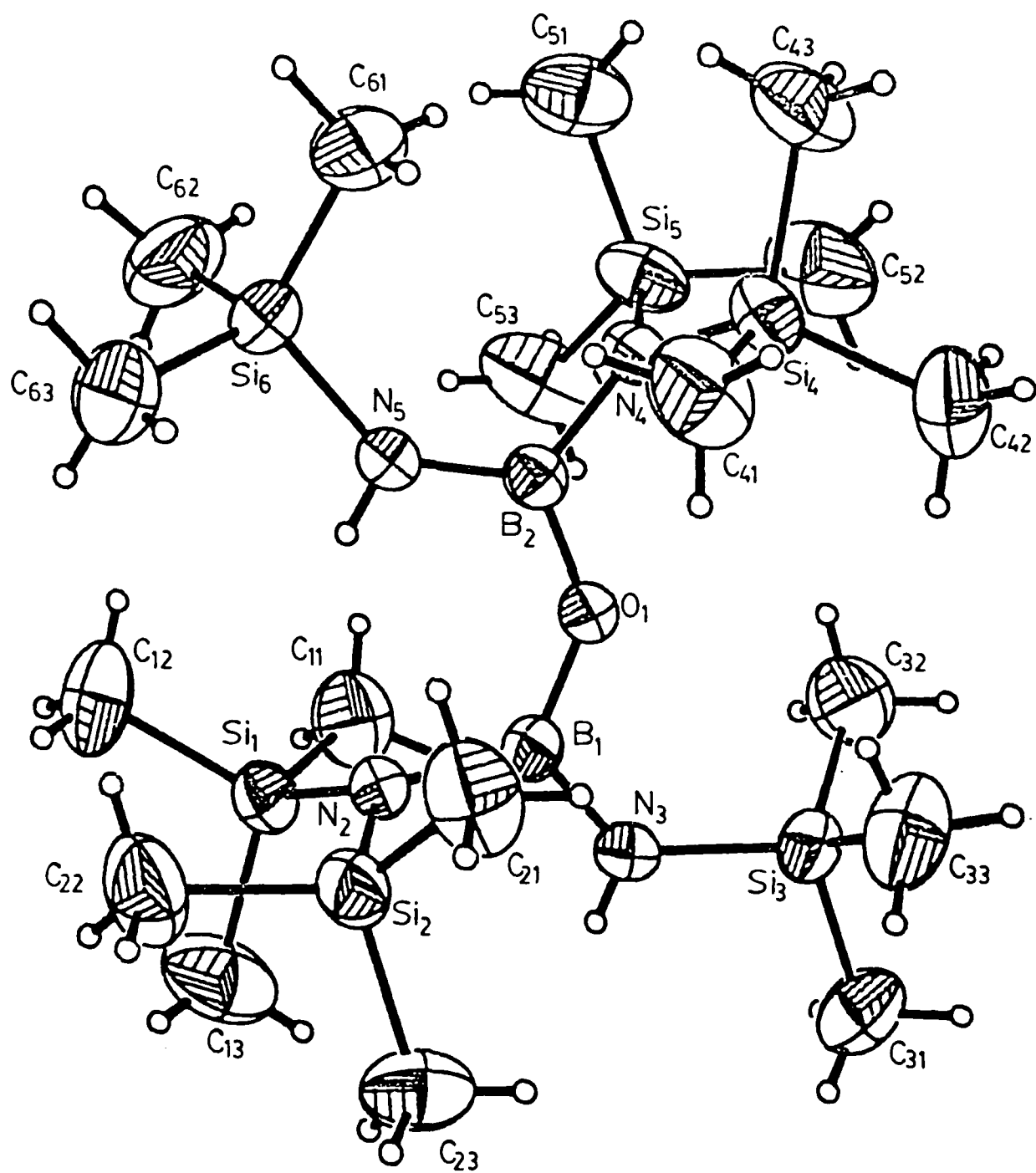
Figure 5. A perspective drawing of  $C_{18}H_{56}N_4OSi_6B_2$  with nonhydrogen atoms represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density; hydrogen atoms are represented by arbitrarily small spheres for purposes of clarity.











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